

PATENT SPECIFICATION

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(54) VINYL CHLORIDE POLYMER COMPOSITIONS AND PRODUCTION THEREOF

(71) We, KUREHA KAGAKU KOGYO KABUSHIKI KAISHA, a joint-stock company of Japan, of 8, 1-chome, Nihonbashi Horidome-cho, Chuo-Ku, Tokyo-To, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to novel vinyl chloride resin compositions having in particular high transparency, high impact resistance, and excellent workability.

A method of improving the impact resistance of products obtained by admixing with polyvinyl chlorides so-called graft copolymers prepared by causing an ethylenically unsaturated monomer or a mixture of two or more such monomers, for example, acrylonitrile, styrene, or methyl methacrylate to undergo graft-polymerisation, is already known.

U. S. Patent No. 2,857,360 discloses the grafting of a monomer mixture of methyl methacrylate-styrene and methyl methacrylate-acrylonitrile to polybutadiene; U. S. Patent No. 3,287,443 discloses the grafting by post-polymerisation of a monomer mixture of methyl methacrylate, acrylonitrile, and styrene onto a butadiene-styrene copolymer; and French Patent No. 1,230,489 discloses the polymerisation of methyl methacrylate by itself on to a synthetic rubber of polybutadiene or butadiene-styrene-methyl methacrylate and the blending of the resulting polymer with polyvinyl chloride for the purpose of improving the quality thereof.

Resin compositions for blending with polyvinyl chloride which are prepared by known processes, however, have many shortcomings and are limited in their applications. For example a certain resin composition may positively improve impact resistance but affects in an undesirable manner the transparent appearance of the product, or another resin composition may affect the transparent appearance of polyvinyl chlorides to a great extent but imparts

in sufficient impact resistance to the product. Furthermore, some compositions have low thermal stabilities and readily undergo discoloration, and the use of certain resin compositions for blending imparts a purplish discoloration to the product. These compositions have the disadvantage of reducing greatly the commercial value of the packaged commodities when used in the production of packaging for food products.

Shaped or formed articles of impact-resistant polyvinyl chlorides of this character are known to develop an extremely milky or whitened appearance in the neighborhood of folds and bends formed in the articles. A further and serious disadvantage of resins for blending known heretofore has been the considerable deviations in the impact strengths of shaped articles according to the processing or working conditions employed. The reason for these deviations is probably the differences due to mixing and kneading in the degree of dispersion of the blending resins within the polyvinyl chloride.

According to the present invention there is provided a vinyl chloride polymer composition of high transparency and high impact resistance comprising in combination:

a. from 1 to 20 percent by weight of a resin prepared by graft-polymerising from 60 to 30 parts by weight of a mixture of monomers comprising styrene, methyl methacrylate and a minor quantity of a cross-linking agent, on coagulated particles of average particle size of from 0.2 to 0.5 micron obtained by adding an acidic substance to a latex containing from 40 to 70 parts by weight of a butadiene polymer or a butadiene-styrene copolymer; the parts by weight of the monomer and polymer used to form the graft polymer totalling 100 and

b. from 99 to 80 percent by weight of a polyvinyl chloride or a copolymer containing vinyl chloride as the principal ingredient thereof.

In accordance with the invention, a polybu-



radlene or polybutadiene-styrene latex preferably having a solids content of from 20 to 50 percent by weight and a pH value of 9.0 or higher and composed of polymer particles 95 percent of which are preferably in the size range of from 0.05 to 0.15 micron is first prepared.

Then, a coagulant is added to this rubber latex to form coagulated rubber particles of an average particle size of from 0.2 to 0.5 micron. In this case, the aggregated or coagulated particle size is the diameter of each coagulated particle formed by the flocculation of spherical polymer particles.

Examples of coagulants which may be added to obtain coagulated particles of uniform average particle size are acidic substances, the addition of which produces remarkably good results when producing uniform coagulated particles. These acidic substances which are mineral acids and organic acids such as hydrochloric acid, sulphuric acid, and nitric acid.

When an acid substance is added as a coagulant, it is necessary to add it gradually to a rubber latex to which a dispersion stabiliser has been added and to lower the pH value of the latex to from 8.5 to 2.0. When the pH value decreases below 2.0, the dispersion stability of the rubber latex becomes poor. For this reason, lumps of the material are formed at a high rate, and precipitation products are undesirably formed in large quantity even at the time of graft-polymerisation. The physical properties of a shaped product produced by blending a blending resin prepared in this manner with a polyvinyl chloride are not readily reproducible. Furthermore, the products obtained contain numerous fish eyes.

The manner in which the dispersion stabiliser and acidic substance are added is also important for obtaining uniform coagulated particles. We have found that sulphonates such as dioctyl ester sulposuccinate and alkylbenzene sulphonates are suitable for use as the dispersion stabiliser when added in a quantity of from 0.05 to 2.0 percent by weight with respect to the solid component.

When more than 2.0 percent by weight of the dispersion stabiliser is added, the coagulating action due to the acidic substance is poor and the impact strength of the resulting resin composition cannot be improved. Moreover, the resin composition has poor thermal stability and tends to become discoloured. On the other hand, when less than 0.05 percent by weight is added, the quantity of resin precipitated when the acidic substance is added is large.

We have found that when an acidic coagulant is added to the rubber latex, a low rubber latex concentration and a low acidic substance concentration produce good results, and it is preferable to carry out the adding of coagulant gradually with uniform agitation.

Before carrying out graft polymerisation of styrene, methyl methacrylate and cross-linking agent on a coagulated rubber latex obtained in the above described manner, it is necessary to return the pH of the emulsion to an alkaline state by adding an aqueous solution of caustic soda or caustic potash.

When carrying out the process of the invention, the proportions of the rubber and plastics components constituting the polymer resins are also important. Of course, if only the impact resistance were to be considered a maximum quantity of the rubber component would be desirable. An extremely large quantity of the rubber component, however, gives rise to the formation of lumps in the acid precipitation or salting-out process and also in the drying process, or has a detrimental effect when the graft copolymer is blended with the polyvinyl chloride so that a uniform dispersion cannot be obtained.

On the other hand, when the content of the rubber component is less than 40 percent by weight, its effect in imparting impact resistance is small, and this rubber component must be blended with the polyvinyl chloride in a large quantity (20 percent by weight or more). Such a procedure is uneconomical and moreover, considerably effects the other physical properties of the polyvinyl chloride.

As a result, the required compositional ratio by weight of the rubber component and the component formed from styrene and methyl methacrylate (the plastics component) is (40 to 70)/(60 to 30).

A homo-polymer of butadiene or a butadiene-styrene copolymer is used as the rubber component, and we have found that a quantity of the styrene in the latter rubber component of less than 30 percent by weight produces good results.

The graft-polymerisation of the plastics component in a quantity of from 60 to 30 parts by weight is carried out by dividing the graft-polymerisation monomer ingredients into from 50 to 90 percent by weight of a monomer mixture of styrene, as the principal constituent, and methyl methacrylate and from 50 to 10 percent by weight of methyl methacrylate alone or in a mixture with styrene, the methyl methacrylate being as the principal constituent. The first mixture is then caused to undergo adsorption polymerisation in the presence of a small quantity of a cross linking agent to form a coagulated rubber latex, and the second mixture is then caused to undergo adsorption polymerisation in the presence of a small quantity of a cross-linking agent.

A substance which copolymerises well with styrene-methyl methacrylate should be used as the cross-linking agent. Examples of such substances are mono-, di-, tri-, and tetraethylene glycol dimethacrylates, 1,3-butyl glycol dimethacrylate, and divinyl benzene. The quantity of the cross-linking agent added is from

0.01 to 5 parts by weight with respect to the monomers.

The polyvinyl chloride which can be used in accordance with the invention are homopolymers produced by known methods such as emulsion polymerisation and suspension polymerisation and, in addition, can be in the form of copolymers or mixtures of 70 percent by weight or more of vinyl chloride and another mono-olefinically unsaturated monomer copolymerisable therewith. 99 to 80 parts by weight of a polyvinyl chloride as defined above and from 1 to 20 parts by weight of the aforementioned resin are then blended together.

The blending can be accomplished, in general, with the materials in powder state by means of mixing machine such as a roll mill or a Banbury mixer. Alternatively, the latex obtained in this invention and the polyvinyl chloride can be blended, and the resulting blend is subjected to salting out or acid precipitation or is spray dried to produce a blended resin composition.

In order that the invention may be more fully understood, the following examples in which all parts and percentages are by weight unless otherwise indicated are given by way of illustration only:—

EXAMPLE 1

A 10-litre, stainless-steel autoclave with agitator was charged with a mixture of 800 grammes (g.) of butadiene, 200 g. of styrene, and 3.0 g. of divinylbenzene, 1.0 g. of potassium persulphate 10.0 g. of potassium oleate, 0.05 g. of EDTA-Sodium salt, 0.5 g. of Rongalite, ("Rongalite" is a registered Trade Mark), 0.03 g. of $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$, and 3,000 g. of distilled water containing 1.5 g. of sodium pyrophosphate. This mixture was caused to react at a temperature of 40 degrees for 17 hours, at which time no further drop in pressure was observable. As a result, a rubber latex having a solids content of 25 percent and a pH value of 9.2 was obtained in a yield of 98 percent.

50 g. of a 2-percent aqueous solution of dioctyl ester sulphasuccinate was added to this latex, and the resulting latex was agitated for 10 minutes, after which a 0.5 aqueous solution of sulphuric acid was added gradually thereto to lower the pH value to 7.0, and the latex was agitated in this state for a further 10 minutes. A 0.5-percent aqueous solution of caustic soda was further added to bring the latex pH value to 10.0.

A mixture of 400 g of styrene containing 8 g. of divinyl benzene and of 200 g. of methyl methacrylate, 0.6 g of potassium persulphate, 0.2 g of Rongalite, and 10 g. of an aqueous solution containing 0.6 g of sodium pyrophosphate were added to this rubber latex. The temperature of the resulting batch was then raised from 40 degrees C to 50 degrees C, and the batch was caused to react for 5 hours. Then 300 g. of methyl methacrylate containing 8 g. of divinyl benzene, 0.3 g. of potas-

sium persulphate, 0.15 g. of Rongalite, and 0.1 g. of sodium pyrophosphate were also added to the latex, and the resulting batch was caused to react for a further 7 hours. The latex thus obtained had a solids content of 38 percent by weight.

This latex was diluted with distilled water until its solid component concentration became 15 percent by weight, and was subjected to acid precipitation at 50 degrees C in the presence of a 1-percent hydrochloric acid solution added thereto. The resulting material was then heat treated at 80 degrees C to coagulate the particles thereof and was then subjected to filtration and drying in air at 70 degrees C. A resin for blending in powder form was obtained in a yield of 98.5 percent by this procedure.

15 parts of this resin were mixed with 85 parts of a polyvinyl chloride of a degree of polymerisation of 800, containing 2 parts of dibutyl tin laurate, and the mixture was kneaded for 3 minutes by rollers at 160 degrees C. The kneaded mixture was then subjected for 5 minutes to a pressure of 150 kg/cm² and at a temperature of 200 degrees C to form a plate of 3-mm. thickness.

The light transmission of this plate was 81.0 percent, and the haze value was 4.5 percent as measured in accordance with the specification of Japanese Industrial Standards, Designation JIS K-6714. Furthermore, a 6-mm. plate obtained the same process as described above was subjected to an Izod impact test with a V notch and found to have an Izod impact strength of 50 kg. cm/cm². When a 1-mm. plate was bent through 90 degrees of angle, almost no white cloudiness was observable.

EXAMPLES 2, 3 and 4.

Resins for blending were prepared by a polymerisation process similar to that set forth in Example 1 except for variations in the pH value in the acid treatment. 15 parts of each resin thus prepared and 85 parts of a polyvinyl chloride were blended to produce a resin composition. The physical properties of these resin compositions designated as Examples 2, 3 and 4 are shown in Table 1, which also indicates in comparative Example 1 the properties of a resin composition obtained without any acid treatment whatsoever.

In the comparative Example 1, in which coagulated particles are not formed, there is a rapid drop in strength when rolled out at relatively high temperature. On the other hand, when a resin was prepared with acid treatment the strength did not drop, particularly, at the high kneading temperature employed but exhibits an unusually high impact strength.

EXAMPLE 5.

A 10-litre, stainless-steel autoclave with an agitator was charged with a mixture of 800 g. of butadiene, 240 g. of styrene, 10.4 g of divinyl benzene, 1.04 g. of potassium persul-

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phate, 10.4 g of potassium oleate, 0.052 g of EDTA-sodium salt, 0.52 g. of Rongalite, 0.031 g. of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and 3,120 g. of distilled water containing 1.73 g. of sodium pyrophosphate. The mixture was caused to react at 40 degrees C for 17 hours, at which time no further drop in pressure was observable. As a result, a rubber latex of a solids content of 25 percent and a pH value of 9.1 was obtained in a polymerisation yield of 98 percent.

15 52 g. of a 2-percent aqueous solution of dioctyl ester sulphosuccinate was added to this latex and the resulting latex was agitated for 10 minutes, after which a 0.5-percent aqueous solution of sulphuric acid was added gradually thereto to lower the pH value to 7.2, and the latex was agitated in this state for a further 10 minutes. An 0.5-percent aqueous solution of caustic soda was then added to the latex to bring its pH value to 10.0.

20 A mixture of 240 g. of styrene containing 1.0 g of divinylbenzene and 200 g. of methyl methacrylate, 0.44 g of potassium persulphate, 0.22 g of Rongalite, and 10 g of an aqueous solution containing 0.66 g. of sodium pyrophosphate were added to this rubber latex. The temperature of the resulting batch was raised from 40 degrees C to 50 degrees C, and the batch was caused to react for 5 hours. Then 120 g. of methyl methacrylate containing 0.3 g. of divinylbenzene, 0.12 g of potassium persulphate, 0.06 g of Rongalite, and 10 g. of an aqueous solution containing 0.12 g. of sodium pyrophosphate were also added to the latex and the resulting composition was caused to react for 7 hours, whereupon a latex having a 34-percent solids content was obtained.

40 This latex was diluted with distilled water until its solids content was 15 percent by weight and, after addition of a 1-percent hydrochloric acid solution was subjected to acid precipitation at 50 degrees C. The resulting material was then heat treated at 80 degrees C to coagulate the particles thereof and was then filtered and dried in dry air at 70 degrees C.

50 15 parts of the resin for blending prepared in the above described manner was blended with 85 parts of a polyvinyl chloride to produce a resin composition having physical properties as indicated in the Table 3.

EXAMPLES 6, 7 and 8.

55 Resins for blending were prepared by polymerisation in accordance with the procedure set forth in example 5 except for variations in the quantity (as indicated in the appended Table 2) of the cross-linking agent added at

the time of graft-polymerisation. 15 parts of each of these resins was admixed with 85 parts of a polyvinyl chloride to produce a resin composition, the physical properties of which are indicated in Table 3.

65 A resin composition sample was produced without the addition of a cross-linking agent at the time of graft-polymerisation and designated as comparative Example 2. As indicated in Table 3, the transparency of this resin composition is poor, and, moreover, considerable whitening occurs at folds in sheets of the resin.

70 The impact strength of a resin composition produced by blending a resin prepared without acid precipitation and a polyvinyl chloride is greatly affected by the kneading temperature employed.

EXAMPLES 9 and 10.

Resins for blending were prepared in accordance with the procedure set forth in Example 5 except that monooctylene glycol dimethacrylate was used instead divinylbenzene as the cross-linking agent and the quantity used was varied. 15 parts of each of the resins thus prepared were blended with 85 parts of a polyvinyl chloride to produce a resin composition having physical properties as indicated in Table 3. Almost no difference in the physical properties of the resin composition due to the change in the cross-linking agent could be discerned.

90 The nature and degree of dispersion in a polyvinyl chloride of the resins for blending with polyvinyl chloride prepared in Example 8 and comparative Example 3 were examined when kneading temperatures of 160 and 175 degrees were employed, by means of an electron microscope. Photographs of the respective results are shown in Figs. 1, 2, 3 and 4 which accompany this specification.

100 In the illustrations, Figs. 1 and 2 are electron microscope photographs showing the character of the resins obtained according to the procedure of Example 8 which were mixed with polyvinyl chloride at kneading temperatures of 160 and 175°C respectively, and Figs. 3 and 4 are similar photographs of the resin obtained in comparative Example 3.

105 The degree of dispersion of the resin for blending prepared in comparative Example 3 differs with the kneading temperature as indicated in Figs 3 and 4, the dispersion units tending to diminish in size with increased temperature. On the other hand, a resin prepared by the method of the invention, wherein the particles are coagulated beforehand by acid treatment, does not exhibit a great variation due to the kneading temperature employed of the size of the dispersion units, as indicated in Figs. 1 and 2.

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TABLE 1

Sample	Acid Treatment pH	Whitening due to Bending	Transparency (%)	"Fish Eyes"	Izod Impact Strength V-notch	
					160°C Roll	175°C Roll
Example 1	7.0	none	81.0	few	50	45
Example 2	6.5	"	80.5	few	52	43
Example 3	4.5	"	80.2	few	68	58
Example 4	2.7	"	79.5	many	85	85
Comparative Example 1	no treatment (9.2)	"	82.0	few	30	4

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TABLE 2

Sample	RUBBER COMPONENT			PLASTICS COMPONENT (first stage post-polymerization)			PLASTICS COMPONENT (second stage post-polymerization)		
	Butadiene (parts)	Styrene (parts)	Divinyl- benzene (parts)	Styrene (parts)	Methyl methacrylate (parts)	Divinyl- benzene (parts)	Methyl methacrylate (parts)	Divinyl- benzene (parts)	
Comparative Example 2	40	12	0.52	12	10	0	6	0	
Example 5	40	12	0.52	12	10	0.05	6	0.015	
Example 6	40	12	0.52	12	10	0.1	6	0.03	
Example 7	40	12	0.52	12	10	0.2	6	0.06	
Example 8	40	12	0.52	12	10	0.07	6	0.03	
Comparative Example 3	40	12	0.52	12	10	0.07	6	0.07	
Example 9	40	12	*0.79	12	10	*0.05	6	*0.023	
Example 10	40	12	*0.79	12	10	*0.10	6	*0.045	

* Monoethylene glycol dimethacrylate used.

TABLE 3

Sample	Treatment pH	Whitening due to Bending	Transparency (%)	"Flash Eyes"	Izod Impact Strength (V notch)	
					160°C Roll	175°C Roll
Comparative Example 2	7.2	excessive	7.5	many	85	75
Example 5	7.2	none	80.0	few	80	73
Example 6	7.2	none	81.8	few	75	65
Example 7	7.2	none	82.0	few	70	62
Example 8	7.2	none	80.0	few	78	67
Comparative Example 3	no treatment (9.2)	none	82.0	few	55	10
Example 9	7.2	none	79.5	few	80	70
Example 10	7.2	none	81.0	few	75	66

WHAT WE CLAIM IS:—

1. A vinyl chloride polymer composition of high transparency and high impact resistance comprising, in combination:

a, from 1 to 20 percent by weight of a resin prepared by graft-polymerizing from 60 to 30 parts by weight of a mixture of monomer comprising styrene, methyl methacrylate and a minor quantity of a cross-linking agent, on coagulated particles of average particle size of from 0.2 to 0.5 micron obtained by adding an acidic substance to a latex containing from 40 to 70 parts by weight of a butadiene polymer or a butadiene-styrene copolymer; the parts by weight of the monomer and polymer used to form the graft polymer totalling 100, and

b. from 99 to 80 percent by weight of a polyvinyl chloride or a copolymer containing vinyl chloride as the principal ingredient thereof.

2. A vinyl chloride polymer composition as claimed in claim 1 in which component a. is a resin prepared by the steps of dividing the mixture of 60 to 30 parts by weight of monomers into from 50 to 90 percent by weight of a first sub-component which is a mixture of styrene, as the principal ingredient, and methyl methacrylate and from 50 to 10 percent by weight of a second subcomponent which is methyl methacrylate or a mixture of styrene and methyl methacrylate, the latter component being the principal ingredient, first causing graft-polymerization of the first sub-component in the presence of a small quantity of a cross-linking agent, on the coagulated particles, and then causing graft-polymerization

of the second subcomponent thereon in the presence of a small quantity of a cross-linking agent.

3. A process for producing a vinyl chloride polymer composition of high transparency and high impact strength, which comprises: adding an acidic substance to a latex containing from 40 to 70 parts by weight of a butadiene polymer or a butadiene-styrene copolymer to produce coagulated particles of average particle size of from 0.2 to 0.5 micron; graft-polymerizing thereon from 60 to 30 parts by weight of monomer comprising styrene, methyl methacrylate and a minor quantity of a cross-linking agent to produce a resin the parts by weight of the monomer and polymer used to form the graft polymer totalling 100, and blending from 1 to 20 percent by weight of the resin with from 99 to 80 percent by weight of a polyvinyl chloride or a copolymer having vinyl chloride as the principal ingredient thereof.

4. A process as claimed in claim 3 for producing a vinyl chloride polymer composition in which the mixture of from 60 to 30 parts by weight of monomers is divided into from 50 to 90 percent by weight of a first subcomponent which is a mixture of styrene, as the principal ingredient, and methyl methacrylate and from 50 to 10 percent by weight of a second subcomponent which is methyl methacrylate or a mixture of styrene and methyl methacrylate the latter component being the principal ingredient; and the first sub-component is then graft-polymerised in the presence of a small quantity of a cross-linking agent; on to the coagulated particles, followed by

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- graft-polymerization of the second sub-component thereon in the presence of a small quantity of a cross-linking agent, to form the resin.
- 5 5. A process as claimed in claim 3 or claim 4 in which the latex to be coagulated with an acidic substance has a solids content of from 20 to 50 percent by weight and a pH value of at least 9.0.
- 10 6. A process as claimed in any one of claims 3 to 5 in which the latex to be coagulated with an acid substance is composed of polymer particles 95% of which are in the size range of 0.05 to 0.15 micron.
- 15 7. A process as claimed in any one of claims 2 to 6 in which the latex contains a dispersion stabilizer.
- 20 8. A process as claimed in claim 7 in which the latex contains from 0.05 to 2.0 percent by weight of a sulphonate as dispersion stabilizer.
9. A process as claimed in claim 8 in which the dispersion stabilizer is dioctylester sulphosuccinate.
10. A process as claimed in claim 8 in which the dispersion stabilizer is an alkylbenzene sulphonate.
11. A process for producing vinyl chloride polymer composition as claimed in claim 3 substantially as hereinafore defined with reference to the Examples.
12. Vinyl chloride polymer compositions when produced by the process claimed in any one of claims 3 to 11.
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1230185 COMPLETE SPECIFICATION

2 SHEETS

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Sheet 1*

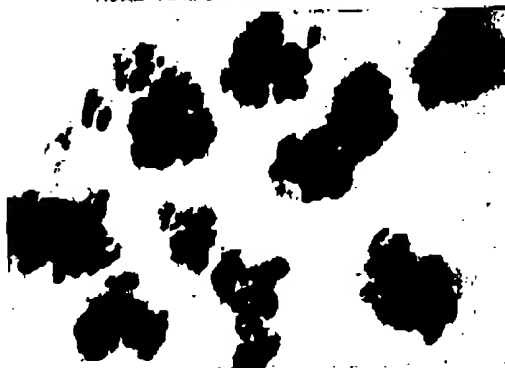
FIG. 1

ROLL TEMPERATURE 160 °C



FIG. 2

ROLL TEMPERATURE 175 °C



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2 SHEETS

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the Original on a reduced scale
Sheet 2*

FIG. 3

ROLL TEMPERATURE 160 °C



FIG. 4

ROLL TEMPERATURE 175 °C

